5-15-2006

10,10′-Dinitro-10,10′-(propane-1,3-diyl)di-10H-anthracen-9-one

Mustafa Arslan
Sakarya University, Adapazari, Turkey

Erol Asker
Balıkesir University, Balıkesir, Turkey

John Masnovi
Cleveland State University, j.masnovi@csuohio.edu

Ronald J. Baker

Recommended Citation

Arslan, M., Asker, E., Masnovi, J., & Baker, R. J. (2006). 10,10?-dinitro-10,10?-(propane-1,3-diyl)di-10H-anthracen-9-one. Acta Crystallographica Section E, 62(5), o2037-o2039. doi:10.1107/S1600536806013705

10,10'-Dinitro-10,10'-(propane-1,3-diyl)di-10H-anthracen-9-one

Mustafa Arslan,[a]* **Erol Asker,**[b] **John Masnovi**[c] **and Ronald J. Baker**[c]

[a]Sakarya Üniversitesi, Fen-Edebiyat Fakültesi Kimya Bölümü, 54140 Esentepe/Adapazarı, Turkey, [b]Balıkesir Üniversitesi, Necatibey Ēğitim Fakültesi, 10100 Balikesir, Turkey, and [c]Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA
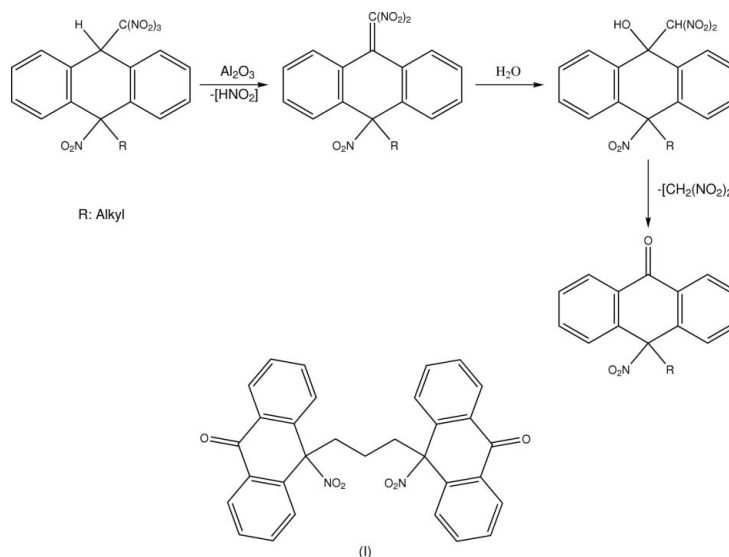
Correspondence e-mail: marslan@sakarya.edu.tr

The title compound, $C_{31}H_{22}N_2O_6$, was obtained as the decomposition product of (E,E)-1,3-bis[9,10-dihydro-9-nitro-10-(trinitromethyl)-9-anthryl]propane, which was synthesized *via* a photochemical reaction of 1,3-di-9-anthrylpropane with tetranitromethane. Intermolecular C—H···O interactions are the most prominent features of the crystal packing; no indications of any intermolecular π–π stacking were found.

Comment

Photonitration of various aromatic compounds using tetranitromethane (TNM) has attracted some attention as an alternative to the conventional nitration processes, which require the use of concentrated nitric and sulfuric acids (Kochi, 1991; Butts *et al.*, 1996; Cox, 1998; Lehnig & Schürmann, 1998). In general, addition of TNM to 9-alkyl-substituted anthracenes proceeds at the 9- and 10-positions, with the nitro group bonding to atom C9, bearing the alkyl group, and the trinitromethyl group being attached to the sterically less hindered unsubstituted C10 center. We have already reported the structure of the product of such a process, (E)-9,10-dihydro-9-methyl-9-nitro-10-(trinitromethyl)anthracene (Arslan *et al.*, 2005). One interesting feature of these trinitromethyl-substituted anthracene derivatives is that they contain the highly labile C—$C(NO_2)_3$ bond and, therefore, when passed through silica gel or an alumina column, easily decompose to form the corresponding anthrone derivatives. The decomposition process is believed to involve retro-aldol reaction.
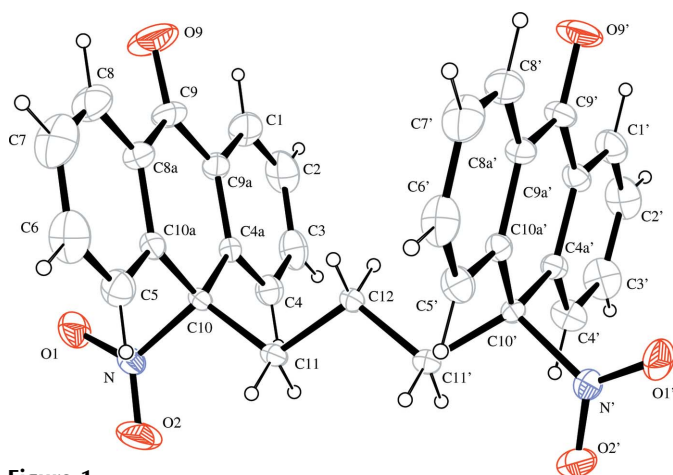
Figure 1
ORTEP (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level. The H atoms are shown as a small circles of arbitrary radii.
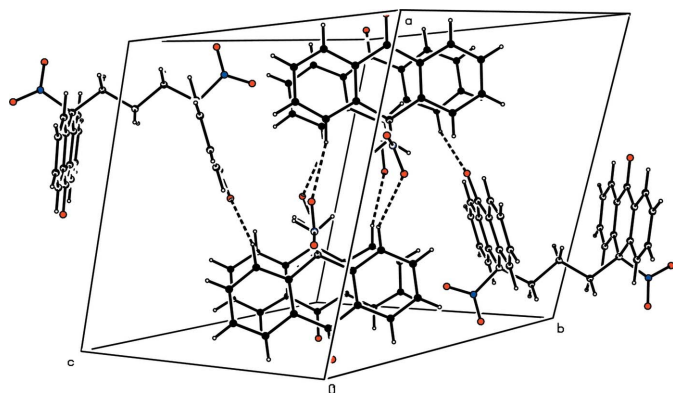

Figure 2
The crystal packing of (I), viewed along the diagonal of the *bc* plane. Dashed lines indicate the C—H···O interactions.

In this paper we report the crystal structure of the title compound, (I), the decomposition product of (*E,E*)-1,3-bis[9,10-dihydro-9-nitro-10-(trinitromethyl)-9-anthryl]propane. The bond lengths and angles in the two anthracene ring systems (Table 1) are in agreement with each other, as well as with those of related compounds (Brinkmann *et al.*, 1970; Rabideau, 1978; Dalling *et al.*, 1981; Arslan *et al.*, 2005).

The 14 atoms of each anthracene system in (I) (Fig. 1) are coplanar to within 0.062 and 0.035 Å for the unprimed and primed ring systems, respectively. The trimethylene chain exhibits an *anti–anti* conformation. The dihedral angle formed by the anthracene planes is 22.51 (9)°.

Examination of the packing diagram (Fig. 2) reveals that the crystal packing is mainly determined by intermolecular C—H···O interactions; there are no indications of intermolecular π–π stacking in the crystal structure of (I).

Experimental

The title compound was obtained as the decomposition product of (*E,E*)-1,3-bis[9,10-dihydro-9-nitro-10-(trinitromethyl)-9-anthryl]-

propane, which was synthesized by irradiation with visual light of a solution containing 20 mg (0.050 mmol) of 1,3-bis(9-anthryl)propane, 325 mg (1.67 mmol) of TNM, 45 ml of pentane, and 5 ml of CCl$_4$ as described by Arslan *et al.* (2005). A 450 W Hanovia medium-pressure mercury lamp with a 500 nm sharp cut-off filter was used as a light source. The (*E,E*)-1,3-bis[9,10-dihydro-9-nitro-10-(trinitromethyl)-9-anthryl]propane was column chromatographed using alumina (80–200 mesh, activity III) as the carrier and dichloromethane–hexane as eluant to give (I) (38.9% yield, m.p. 464–465 K). Single crystals suitable for X-ray diffraction study were grown from a concentrated solution of (I) in dichloromethane through slow evaporation under ambient conditions.

Crystal data

$C_{31}H_{22}N_2O_6$	$Z = 4$
$M_r = 518.51$	$D_x = 1.343$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.438$ (2) Å	$\mu = 0.09$ mm^{-1}
$b = 14.490$ (3) Å	$T = 295$ (2) K
$c = 13.974$ (3) Å	Block, yellow
$\beta = 109.505$ (5)°	$0.32 \times 0.29 \times 0.13$ mm
$V = 2564.8$ (9) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	1912 reflections with $I > 2\sigma(I)$
ω scans	$\theta_{max} = 25.1°$
Absorption correction: none	3 standard reflections
4554 measured reflections	every 120 min
4554 independent reflections	intensity decay: 1.1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.076$	$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2]$
$wR(F^2) = 0.214$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
4554 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
352 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N	1.187 (5)	O2′—N′	1.210 (5)
O2—N	1.175 (5)	O9′—C9′	1.221 (5)
O9—C9	1.228 (5)	N—C10	1.554 (5)
O1′—N′	1.185 (4)	N′—C10′	1.558 (5)
O1—N—O2	122.4 (4)	C4A—C10—N	105.5 (3)
O1—N—C10	117.6 (4)	C10A—C10—N	105.0 (3)
O2—N—C10	120.0 (4)	C11—C10—N	107.6 (3)
O1′—N′—O2′	123.4 (4)	C11′—C10′—C10A′	111.6 (4)
O1′—N′—C10′	118.7 (4)	C11′—C10′—C4A′	111.9 (3)
O2′—N′—C10′	117.6 (4)	C10A′—C10′—C4A′	115.5 (3)
C4A—C10—C10A	115.1 (3)	C11′—C10′—N′	107.9 (3)
C4A—C10—C11	111.2 (4)	C10A′—C10′—N′	105.2 (3)
C10A—C10—C11	111.7 (4)	C4A′—C10′—N′	104.0 (3)
O2—N—C10—C10A	−116.4 (6)	O1′—N′—C10′—C11′	−164.3 (4)
O1—N—C10—C11	−175.4 (4)	O2′—N′—C10′—C11′	21.6 (5)
N—C10—C11—C12	178.1 (4)	C11—C12—C11′—C10′	178.4 (4)
C10—C11—C12—C11′	179.1 (4)	N′—C10′—C11′—C12	178.5 (4)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2′—H2′⋯O2^i	0.93	2.67	3.586 (10)	168
C4—H4⋯O9^{ii}	0.93	2.60	3.417 (6)	147
C5—H5⋯O2′^{iii}	0.93	2.69	3.363 (7)	130
C5′—H5′⋯O2^{iii}	0.93	2.53	3.343 (7)	146
C7′—H7′⋯O2′^{iv}	0.93	2.57	3.473 (7)	165

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y+1, -z+3$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

All H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms at C—H distances of 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Arslan, M., Baker, R. J., Masnovi, J. & Asker, E. (2005). *Acta Cryst.* E**61**, o4133–o4135.

Brinkmann, A. W., Gordon, M., Harvey, R. G., Rabideau, P. W., Stothers, J. B. & Terney, A. L. (1970). *J. Am. Chem. Soc.* **92**, 5912–5916.

Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T., Timmerman-Vaughan, D. J. & Young, D. A. W. (1996). *Acta Chem. Scand.* **50**, 29–47.

Cox, A. (1998). *Photochemistry*, **29**, 164–203.

Dalling, D. K., Zilm, K. W., Grant, D. M., Heeschen, W. A., Horton, W. J. & Pugmire, R. J. (1981). *J. Am. Chem. Soc.* **103**, 4817–4824.

Enraf–Nonius (1993). *CAD-4-PC Software*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Kochi, J. K. (1991). *Pure Appl. Chem.* **63**, 255–264.

Lehnig, M. & Schürmann, K. (1998). *Eur. J. Org. Chem.* pp. 913–918.

Rabideau, P. W. (1978). *Acc. Chem. Res.* **11**, 145–147.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.